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| (54) Title: HYDROGENATION PROCESS | | | |
| (57) Abstract | | | |
| <p>A hydrogenation process for the production of a food grade white oil uses a catalyst which is based on an ultra-large pore crystalline material. The crystalline material has pores of at least 13 Å diameter arranged in a uniform manner and exhibits unusually large sorption capacity demonstrated by its benzene adsorption capacity of greater than about 15 grams benzene/100 grams (50 torr and 25 °C). A preferred form of the catalyst has a hexagonal structure which exhibits a hexagonal electron diffraction pattern that can be indexed with a d₁₀₀ value greater than about 18 Å. The hydrogenation catalysts based on these materials are capable of reducing the unsaturation in lubricants to a low level to produce a food grade white oil, employing less severe conditions than catalysts of the prior art.</p> | | | |

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HYDROGENATION PROCESS

This invention relates to a process for hydrogenating lubricant oils to produce food grade white oils.

There is a significant commercial demand for oils known as food grade mineral oils, or white oils. In addition to food preparation, they are also used in the manufacture of paper and textiles. Such oils also have medicinal uses. These oils are referred to as "white", but they are actually colorless or very light in color.

The preparation of white oils is well-known. These oils have stringent API gravity and viscosity requirements. They must have an API gravity between 29 and 32. The kinematic viscosity of white oils is between 10 and 600 cS at 56°C (100°F). The Saybolt Universal Viscosity of white oils which is the preferred viscosity range is between 26 and 140 (76-296 cS) at 56°C (100°F). The most preferred viscosities are in the lower end of this range. The flash point is between 125 and 195°C (260 and 380°F). The boiling range of white oil is between 260 and 705°C (500°F and 1300°F). White oils must meet or exceed strict test requirements on sulfur, readily carbonizable substances and ultraviolet absorbance. The standards for white oil which may be safely used in food are established by the Food and Drug Administration and are set forth in 21 CFR §172.878.

White oils are generally produced by the hydrogenation or hydrotreating of lubricant oils under severe conditions. Hydrogenation is a well-established process both in the chemical and petroleum refining industries. Hydrogenation is conventionally carried out in the presence of a catalyst which usually comprises a metal hydrogenation component on a porous support material, such as a natural clay or a synthetic oxide. Metals such as nickel, platinum, palladium and combinations of metals are often used. Typical support materials include kieselguhr, alumina, silica and silica-alumina. Depending upon the ease with which the feed may be hydrogenated, the hydrogen pressures used may vary from quite low to very high values, typically

from 3550 to 21,000 kPa (500 to 3,000 psig). Hydrogenation is an exothermic process and is therefore thermodynamically favored by lower temperatures but for kinetic reasons, moderately elevated temperatures are normally used and for 5 petroleum refining processes, temperatures in the range of 120 to 370°C (250° to 700°F) are typical. Space velocity may range from 0.1 to 2.0 LHSV.

Hydrogenative treatment is frequently used in 10 petroleum refining to improve the qualities of lubricating oils, both of natural mineral oil and synthetic origin. Hydrogenation, or hydrotreating as it is frequently termed, is used to reduce any residual unsaturation in the lubricating oil, to remove heteroatom-containing impurities and color bodies. In mineral oils, the removal of 15 impurities and color bodies is of particular significance, especially for mineral oils which have been subjected to hydrocracking or catalytic dewaxing. For both mineral and synthetic stocks, the saturation of lube boiling range olefins or aromatics is a major objective.

White oils have traditionally been prepared by 20 hydrotreating the lubricant oil fraction of the hydrocracker effluent under conditions of extreme severity, i.e., high pressures and low space velocities. Hydrotreating units often operate at metallurgical pressure 25 limits and low throughputs to produce white oils. The prior art discloses the preparation of white oils using hydrogenation techniques. In many of these cases the catalyst employed comprises Pt or Pd combined in some manner with a non-acidic refractory inorganic oxide 30 material such as alumina. Nickel in some cases may also be employed as the hydrogenation component. U.S. Patent No. 5,057,206 discloses the production of a white oil from a heavy alkylate feedstock possessing hydrogenatable components. The catalyst employed is a Pt group metal 35 compound that has been surface impregnated upon an alumina support.

U.S. Patent No. 4,240,900 discloses a process for the hydrogenation of olefins and aromatic compounds, useful in the production of white oils, employing a zeolite-containing catalyst that has been treated with a hydrocarbon stream relatively high in organic nitrogen compounds in order to suppress its cracking activity. Nickel is a preferred hydrogenation component in this patent.

U.S. Patent No. 3,926,777 combines hydrogenation with solvent dewaxing to produce a colorless mineral oil with good hazing properties. This patent involves more than one hydrogenation step with more than one catalyst. The catalysts comprise a combination of a Group VIB metal and a Group VIII metal on a non-acidic or weakly acidic support, and a Group VIII metal alone on a non-acidic or weakly acidic support.

The catalysts used for hydrogenating lubricants, whether of mineral or of synthetic origin, require a strong hydrogenation function provided by the metal component and large pore diameters in the porous support material in order to minimize the diffusion resistance of the bulky lubricant molecules. For reactions with bulky molecules, the optimum ratio of catalytic pore diameter to molecule size is about 1.5:1. Table 1 below shows the optimum pore sizes required for normal alkanes in the C-7 to C-25 range. The table shows that for alkanes in this range, the chain-length varies from 9.9 to 37.6 Å so that active hydrogenation catalysts for these materials should have a major amount of their pore volume with pore openings in the range of 15 to 56 Å, and preferably with a major amount of this in the range 38 to 56 Å.

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TABLE 1
OPTIMUM PORE SIZE

| <u>Carbon Number</u> | <u>Alkane Length, Å (1)</u> | <u>Optimum Pore Diameter, Å (2)</u> |
|----------------------|-----------------------------|-------------------------------------|
| 5 | C ₇ 9.9 | 15 |
| | C ₈ 11.5 | 17 |
| | C ₁₀ 14.5 | 22 |
| | C ₁₂ 17.6 | 26 |
| 10 | C ₁₇ 25.3 | 38 |
| | C ₁₉ 28.4 | 43 |
| | C ₂₁ 31.5 | 47 |
| | C ₂₃ 34.6 | 52 |
| | C ₂₅ 37.6 | 56 |

1. Based on bond lengths of 1.54 and 1.11 Å for C-C and C-H bond lengths, respectively.
- 15 2. Based on an optimum ratio of catalyst pore to molecule size ratio of 1.5.

Conventional amorphous support materials such as alumina, silica and silica-alumina, typically have a pore size distribution with most of the pores larger than 50 Å and most of these are larger than 100 Å. Although these large pores enable the bulky lubricant molecules to traverse the molecular structure of the catalyst freely with little diffusion resistance, the reduced surface area associated with the larger pore sizes diminishes the area which is available for the hydrogenation reactions. It would therefore be desirable to utilize a hydrogenation catalyst which posses a significant amount of its pores in the range of 15 to 60 Å, close to the optimum ratio for the lower molecular weight materials making up the bulk of many synthetic lubricants as well as the lower viscosity mineral oils.

As stated previously, hydrotreating units commonly operate at metallurgical pressure limits and low throughputs to produce white oils. Operation at high severities is quite expensive. Furthermore, if the hydrogenation catalyst is nickel-based rather than based on

a noble metal, the catalyst can be irreversibly poisoned by sulfur.

As is indicated by the prior art, many hydrotreating units employ nickel based catalysts. Such catalysts have 5 low sulfur tolerances relative to noble metals.

Furthermore, nickel catalysts require special handling and disposal methods due to their toxic nature. A noble metal catalyst may be potentially regenerated and reused.

Ability to operate at higher throughput or lower pressures 10 (i.e., lower severity) can result in savings by debottlenecking existing units or lowering metallurgical requirements and capital cost for grass roots designs.)

We have now found that another class of catalytic materials, the mesoporous crystalline materials (known 15 collectively as M41S) which have high pore volume, high surface area and controlled pore openings of at least 13 Å, is particularly suitable for the hydrogenation of lubricant hydrocarbons for the production of food grade white oils. These catalysts are disclosed in U.S. Patent Nos. 5,108,725 20 (Beck et al), 5,102,643 (Kresge et al) and 5,098,684 (Kresge et al). Hydrogenation employing mesoporous crystalline materials has now been found to provide white oil of equal or superior quality and equal or superior yield at less severe conditions than hydrogenation 25 employing catalysts of the prior art. The incorporation of noble metals on mesoporous crystalline catalysts has also produced an improvement in noble metal activity beyond that seen when these metals were incorporated onto catalysts of the prior art. It has also been found that the level of 30 aromatics in the white oil product can be substantially reduced when noble metals incorporated onto mesoporous crystalline catalysts are used as opposed to noble metals on alumina catalyst, as the examples below illustrate.

According to the present invention, therefore, there is 35 provided a process for hydrogenating a lubricant hydrocarbon to produce a food grade white oil, said process

comprising contacting a hydrocarbon lubricant feed in the presence of hydrogen with a hydrogenation catalyst containing a metal hydrogenation catalyst on a support, the support comprising an inorganic, non-layered, porous, 5 crystalline phase material having pores with diameters of at least about 13 Å and exhibiting, after calcination, an X-ray diffraction pattern with at least one d-spacing greater than about 18 Å with a relative intensity of 100.

In a preferred form, the support material is 10 characterized by a substantially uniform hexagonal honeycomb microstructure with uniform pores having a cell diameter greater than 13 Å and typically in the range of 20 to 100 Å. Most prominent among these materials is a new crystalline material identified as MCM-41 which is usually 15 synthesized as a metallosilicate with Brønsted acid sites by incorporating a tetrahedrally coordinated trivalent element such as Al, Ga, B, or Fe within the silicate framework. The preferred forms of these materials are the aluminosilicates although other metallosilicates may also 20 be utilized.

A preferred catalyst for the present purpose is an alumina bound crystalline material which has a significant pore volume with pore diameters greater than 200 Å. The large diameter pores provide channels for bulky lubricant 25 molecules to transport freely with diminished diffusion resistance to the smaller particles of the crystalline material which provide a large surface area for the hydrogenation reaction. The preferred crystalline materials for use in the present process have pore 30 diameters greater than 15 Å and the preferred pore diameters are in the range of 15 to 60 Å. The crystalline (i.e. meant here as having sufficient order to provide, after calcination, a diffraction pattern with at least one peak by, for example, X-ray, electron or neutron 35 diffraction) support material of this invention is generally "mesoporous", by which is meant that the material

has uniform pores of diameter within the range of 1.3 to 20 nm. More preferably, the materials of the invention have uniform pores of diameter within the range 1.8 to 10 nm. In this respect, pore size is considered as the maximum 5 perpendicular cross-sectional dimension of the pore.

The support material of the present invention can be distinguished from other porous inorganic solids by the regularity of its large open pores, whose size more nearly resembles that of amorphous or paracrystalline materials, 10 but whose regular arrangement and uniformity of size (pore size distribution within a single phase of, for example, \pm 25%, usually \pm 15% or less of the average pore size of that phase) more closely resemble those of crystalline framework materials such as zeolites.

15 In the preferred arrangement, the porosity of the crystalline support material of the invention is provided by a generally hexagonal arrangement of open channels, a property that can be readily observed by electron diffraction and transmission electron microscopy. In particular, the transmission electron micrograph of 20 properly oriented specimens of the material show a hexagonal arrangement of large channels and the corresponding electron diffraction pattern gives an approximately hexagonal arrangement of diffraction maxima.

25 The d_{100} spacing of the electron diffraction patterns is the distance between adjacent spots on the hko projection of the hexagonal lattice and is related to the repeat distance a_0 between channels observed in the electron micrographs through the formula $d_{100} = a_0 \sqrt{3}/2$. This d_{100} spacing observed in the electron diffraction patterns 30 corresponds to the d-spacing of a low angle peak in the x-ray diffraction pattern of the material. The most highly ordered preparations of the material obtained so far have 20-40 distinct spots observable in the electron diffraction 35 patterns. These patterns can be indexed with the hexagonal

hk0 subset of unique reflections of 100, 110, 200, 210, etc., and their symmetry-related reflections.

In this respect, it is to be understood that the reference to a hexagonal arrangement of channels is intended to encompass not only mathematically perfect hexagonal symmetry but also an arrangement in which most channels in the material are surrounded by six nearest neighbor channels at substantially the same distance. Defects and imperfections will cause significant numbers of channels to violate this criterion to varying degrees. Samples which exhibit as much as \pm 25% random deviation from the average repeat distance between adjacent channels still clearly give recognizable images of the present ultra-large pore materials.

In its calcined form, the crystalline support material of the invention may be further characterized by an X-ray diffraction pattern with at least one peak at a position greater than about 1.8 nm d-spacing (4.909 degrees two-theta for Cu K-alpha radiation) which corresponds to the d_{100} value of the electron diffraction pattern of the material.

More preferably, the calcined crystalline support material of the invention is characterized by an X-ray diffraction pattern with at least two peaks at positions greater than about 1 nm d-spacing (8.842 degrees two-theta for Cu K-alpha radiation), at least one of which is at a position greater than 1.8 nm d-spacing, and no peaks at positions less than 1 nm d-spacing with relative intensity greater than about 20% of the strongest peak. Still more particularly, the X-ray diffraction pattern of the calcined material of this invention has no peaks at positions less than 1 nm d-spacing with relative intensity greater than about 10% of the strongest peak. In the preferred hexagonal arrangement, at least one peak in the X-ray pattern will have a d-spacing corresponding to the d_{100} value of the electron diffraction pattern of the material.

X-ray diffraction data referred to herein were collected on a Scintag PAD X automated diffraction system employing theta-theta geometry, Cu K-alpha radiation, and an energy dispersive X-ray detector. Use of the energy dispersive X-ray detector eliminated the need for incident or diffracted beam monochromators. Both the incident and diffracted X-ray beams were collimated by double slit incident and diffracted collimation systems. The slit sizes used, starting from the X-ray tube source, were 0.5, 1.0, 0.3 and 0.2 mm, respectively. Different slit systems may produce differing intensities for the peaks. The materials of the present invention that have the largest pore sizes may require more highly collimated incident X-ray beams in order to resolve the low angle peak from the transmitted incident X-ray beam.

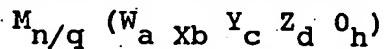
The diffraction data were recorded by step-scanning at 0.04 degrees of two-theta, where theta is the Bragg angle, and a counting time of 10 seconds for each step. The interplanar spacings, d's, were calculated in nanometers (nm), and the relative intensities of the lines, I/I_0 , where I_0 is one-hundredth of the intensity of the strongest line, above background, were derived with the use of a profile fitting routine. The intensities were uncorrected for Lorentz and polarization effects. The relative intensities are given in terms of the symbols vs = very strong (75-100), s = strong (50-74), m = medium (25-49) and w = weak (0-24). It should be understood that diffraction data listed as single lines may consist of multiple overlapping lines which under certain conditions, such as very high experimental resolution or crystallographic changes, may appear as resolved or partially resolved lines. Typically, crystallographic changes can include minor changes in unit cell parameters and/or a change in crystal symmetry, without a substantial change in structure. These minor effects, including changes in relative intensities, can also occur as a result of

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differences in cation content, framework composition, nature and degree of pore filling, thermal and/or hydrothermal history, and peak width/shape variations due to particle size/shape effects, structural disorder or 5 other factors known to those skilled in the art of X-ray diffraction.

The support material of the invention preferably exhibits an equilibrium benzene adsorption capacity of greater than about 15 grams benzene/100 grams crystal at 10 6.7 kPa (50 torr) and 25°C. The equilibrium benzene adsorption capacity must, of course, be measured on a sample which exhibits no pore blockage by incidental contaminants. For example, water should be removed by dehydration techniques, e.g. thermal treatment, whereas 15 inorganic amorphous materials, e.g. silica, and organics should be removed by contact with acid or base or other chemical agents and/or physical methods (such as, calcination) so that the detrital material is removed without detrimental effect on the material of the 20 invention.

In general, crystalline support material of this invention has the following composition:



wherein W is a divalent element, such as a divalent first 25 row transition metal, e.g. manganese, cobalt, nickel, iron, and/or magnesium, preferably cobalt; X is a trivalent element, such as aluminum, boron, chromium iron and/or gallium, preferably aluminum; Y is a tetravalent element such as silicon and/or germanium, preferably silicon; Z is 30 a pentavalent element, such as phosphorus; M is one or more ions, such as, for example, ammonium, Group IA, IIA and VIIIB ions, usually hydrogen, sodium and/or fluoride ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q 35 is the number of moles or mole fraction of M; a, b, c, and

d are mole fractions of W, X, Y and Z, respectively; h is a number of from 1 to 2.5; and (a+b+c+d) = 1.

A preferred embodiment of the above crystalline material is when (a+b+c) is greater than d, and h = 2.

5 More preferably, when h = 2, a = 0 and d = 0.

In the as-synthesized form, the support material of this invention has a composition, on an anhydrous basis, expressed empirically as follows:



10 wherein R is the total organic material used to assist in the synthesis of the material and not included in M as an ion, and r is the coefficient for R, i.e. the number of moles or mole fraction of R.

15 The M and R components are associated with the material as a result of their presence during crystallization, and are easily removed or, in the case of M, replaced by post-crystallization methods hereinafter more particularly described. For example, the original M, e.g. sodium or chloride, ions of the as-synthesized material of this 20 invention can be replaced by ion exchange with other ions.

Preferred replacing ions include metal ions, hydrogen ions, hydrogen precursor, e.g. ammonium, ions and mixtures thereof.

Support materials having the composition defined by the 25 above formula can be prepared from a reaction mixture having a composition in terms of mole ratios of oxides, within the following ranges:

| | <u>Reactants</u> | <u>Useful</u> | <u>Preferred</u> |
|----|---|---------------|------------------|
| | X_2O_3/YO_2 | 0 to 0.5 | 0.001 to 0.5 |
| | $X_2O_3/(YO_2+Z_2O_5)$ | 0.1 to 100 | 0.1 to 20 |
| | $X_2O_3/(YO_2+WO+Z_2O_5)$ | 0.1 to 100 | 0.1 to 20 |
| 5 | Solvent/ $(YO_2+WO+Z_2O_5+X_2O_3)$ | 1 to 1500 | 5 to 1000 |
| | OH^-/YO_2 | 0 to 10 | 0 to 5 |
| | $(M_2/e^{O+R}/f^O)/(Y_2^{O+}W_2O_5+X_2O_3)$ | 0.01 to 20 | 0.05 to 5 |
| | $M_2/e^{O+}/(YO_2+WO+Z_2O_5+X_2O_3)$ | 0 to 10 | 0 to 5 |
| 10 | $R_2/f^O/(YO_2+WO+Z_2O_5+X_2O_3)$ | 0.01 to 2.0 | 0.03 to 1.0 |

wherein e and f are the weighted average valences of M and R, respectively, wherein the solvent is a C_1 to C_6 alcohol or diol, or, more preferably, water and wherein R comprises an organic directing agent having the formula $R_1R_2R_3R_4Q+$ 15 wherein Q is nitrogen or phosphorus and wherein at least one of R_1 , R_2 , R_3 and R_4 is aryl or alkyl group having 6 to 36 carbon atoms, e.g. $-C_6H_{13}$, $-C_{10}H_{21}$, $-C_{16}H_{33}$ and $-C_{18}H_{37}$, and each of the remainder of R_1 , R_2 , R_3 and R_4 is selected from hydrogen and an alkyl group having 1 to 5 20 carbon atoms. The compound from which the above ammonium or phosphonium ion is derived may be, for example, the hydroxide, halide, silicate or mixtures thereof.

The particular effectiveness of the above directing agent, when compared with other such agents known to direct 25 synthesis of one or more other crystal structures, is believed due to its ability to function as a template in the nucleation and growth of the desired ultra-large pore materials. Non-limiting examples of these directing agents include cetyltrimethylammonium, cetyltrimethylphosphonium, octadecyltrimethylphosphonium, benzyltrimethylammonium, 30 cetylpyridinium, myristyltrimethylammonium,

decyltrimethylammonium, dodecyltrimethylammonium and dimethyldodecylammonium compounds.

Preferably, the total organic, R, present in the reaction mixture comprises an additional organic directing agent in the form of an ammonium or phosphonium ion of the above directing agent formula but wherein each R_1 , R_2 , R_3 and R_4 is selected from hydrogen and an alkyl group of 1 to 5 carbon atoms (2 of the alkyl groups can be interconnected to form a cyclic compound). Examples of the additional organic directing agent include tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium and pyrrolidinium compounds. The molar ratio of the first-mentioned organic directing agent to the additional organic directing agent can be in the range 100/1 to 0.01/1. Where the additional organic directing agent is present, the molar ratio $R_2/fO/(Y_{O_2}+W_{O_2}+Z_{2O_5}+X_{2O_3})$ in the reaction mixture is preferably 0.1 to 2.0, most preferably 0.12 to 1.0.

In addition, to vary the pore size of the final crystalline phase material, the total organic, R, in the reaction mixture can include an auxiliary organic in addition to the organic directing agent(s) described above. This auxiliary organic is selected from (1) aromatic hydrocarbons and amines having 5-20 carbon atoms and halogen- and C_1-C_{14} alkyl-substituted derivatives thereof, (2) cyclic and polycyclic aliphatic hydrocarbons and amines of 5 to 20 carbon atoms and halogen- and C_1-C_{14} alkyl-substituted derivatives thereof and (3) straight and branched chain aliphatic hydrocarbons and amines having 3-16 carbon atoms and halogen-substituted derivatives thereof.

In the above auxiliary organics, the halogen substituent is preferably bromine. The C_1-C_{14} alkyl substituent may be a linear or branched aliphatic chain, such as, for example, methyl, ethyl, propyl, isopropyl, butyl, pentyl and combinations thereof. Examples of these

auxiliary organics include, for example, p-xylene, trimethylbenzene, triethylbenzene and triisopropylbenzene.

With the inclusion of the auxiliary organic in the reaction mixture, the mole ratio of auxiliary organic/YO₂ will be from 0.05 to 20, preferably from 0.1 to 10, and the mole ratio of auxiliary organic/organic directing agent(s) will be from 0.02 to 100, preferably from 0.05 to 35.

When a source of silicon is used in the synthesis method, it is preferred to use at least in part an organic silicate, such as, for example, a quaternary ammonium silicate. Non-limiting examples of such a silicate include tetramethylammonium silicate and tetraethylorthosilicate.

Non-limiting examples of various combinations of W, X, Y and Z contemplated for the above reaction mixture include:

| | W | X | Y | Z |
|----|----|----|----|----|
| | -- | Al | Si | -- |
| | -- | Al | -- | P |
| | -- | Al | Si | P |
| 20 | Co | Al | -- | P |
| | Co | Al | Si | P |
| | -- | -- | Si | -- |

including the combinations of W being Mg, or an element selected from the divalent first row transition metals, e.g. Mn, Co and Fe; X being B, Ga or Fe; and Y being Ge.

To produce the crystalline support material of the invention, the reaction mixture described above is maintained at a temperature of 25 to 250°C, preferably 50 to 175°C, and preferably a pH of 9 to 14 for a period of time until the required crystals form, typically 5 minutes to 14 days, more preferably 1 to 300 hours.

When the crystalline material of the invention is an aluminosilicate, the synthesis method conveniently involves the following steps:

(1) Mix the organic (R) directing agent with the solvent or solvent mixture such that the mole ratio of solvent/ $R_{2/f}^0$ is within the range of 50 to 800, preferably from 50 to 500. This mixture constitutes the "primary template" for the synthesis method.

(2) To the primary template mixture of step (1), add the silica and alumina such that the ratio of $R_{2/f}^0/(SiO_2+Al_2O_3)$ is within the range 0.01 to 2.0.

(3) Agitate the mixture resulting from step (2) at a temperature of 20 to 40°C, preferably for 5 minutes to 3 hours.

(4) Allow the mixture to stand with or without agitation, preferably at 20 to 50°C, and preferably for 10 minutes to 24 hours.

(5) Crystallize the product from step (4) at a temperature of 50 to 150°C, preferably for 1 to 72 hours.

When used as a support material, the composition of the invention should be subjected to treatment to remove part or all of any organic constituent. Typically, this involves thermal treatment (calcination) at a temperature of 400 to 750°C for at least 1 minute and generally not longer than 20 hours, preferably from 1 to 10 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience, such as in air, nitrogen and ammonia.

In the present process, lubricant range hydrocarbons are hydrogenated or hydrotreated in the presence of a hydrogenation catalyst which comprises the above-described mesoporous crystalline material, preferably with a binder which possesses a significant pore volume having pore diameters greater than 200 Å. The process may be carried out with mineral oil lubricants or synthetic hydrocarbon lubricants. The properties of the feed of the instant application are disclosed in Table 2.

The mineral oil lubricants may generally be characterized as having a minimum boiling point of at least

500°F. (about 260°C) and usually they will be neutral i.e., distillate stocks with an end point of not more than 1000°F. (about 540°C), although residual lube stocks such as bright stock may also be treated by the same catalytic process. Hydroprocessed Light Neutral basestock is useful in the instant invention. Higher viscosity feedstocks low in sulfur are also suitable. Mineral oil stocks of this kind are typically prepared by the conventional refining process involving atmospheric and vacuum distillation of a crude of suitable composition, followed by removal of undesirable aromatic components by solvent extraction using a solvent such as phenol, furfural or N,N-dimethylformamide (DMF). Dewaxing to the desired product pour point may be carried out using either solvent dewaxing or catalytic dewaxing techniques and it is particularly preferred that a hydrogenative treatment according to the present invention should follow any catalytic dewaxing treatment in order to saturate lube boiling range olefins which may be produced during the catalytic dewaxing process.

20 The lubricant material is initially hydrotreated using a commercial catalyst such as nickel and molybdenum impregnated on Al_2O_3 then subjected to the hydrogenative treatment in the presence of a catalyst which comprises a metal component for hydrogenation together with the mesoporous crystalline material and, optionally, a binder. The metal component will normally be selected from Groups VIA, VIIA and VIIIA of the Periodic Table, such as Pt, Pd, or Ni. The amount of hydrogenation metal on the mesoporous support will depend on the type of metal employed. In the preferred case of a noble metal, the catalyst will normally contain less than 1 wt% of the metal. However with a non-noble metal, such as nickel, the catalyst will normally contain 5-20 wt% metal.

35 The hydrogenation reaction is carried out under conditions of lower severity than those employed with conventional catalysts with temperatures from 120-370°C

(250-700°F), preferably 230-290°C (450-550°F), and pressures of 3550 to 20800 kPa (500 to 3000 psig). Hydrogen circulation rates are typically in the range 180 to 900 Nm₃/m₃ (1,000 to 5,000 scf/bbl) and once through circulation is preferred in order to maximize the purity of the hydrogen. Space velocities are typically in the range of 0.1 to 2.0 LHSV, usually from 0.3 to 0.5 LHSV. The products of the hydrogenation reaction have a low degree of unsaturation consistent with the hydrogenative treatment.

The invention will now be more particularly described with reference to the Examples and the accompanying drawings, in which Figures 1, 2 and 3 are graphical representations of testing results presented in Table 4.

In the Examples, percentages are by weight unless otherwise indicated.

EXAMPLE 1

Pd/M41S Catalyst Preparation

A sample of a mesoporous crystalline material (40Å) was prepared in accordance with the method described below.

The following mixture was charged to an autoclave:

| | |
|---------|---|
| 60.7pbw | Cetyltrimethylammonium (CTMA) |
| | hydroxide, prepared by contacting a |
| | 29wt.% N,N,N-trimethyl-1- |
| | hexadecylammonium chloride solution |
| 25 | with a hydroxide-for-halide exchange |
| | resin |
| 1.3pbw | Sodium aluminate, |
| 30.4pbw | Tetramethylammonium silicate (10% |
| | aqueous solution), |
| 30 | 7.6pbw Precipitated hydrated silica (HiSil™). |

The mixture was crystallized at 100°C for 20 hrs. with stirring under autogenous pressure. The resulting product was recovered by filtration and dried in air at ambient temperature. A sample of the product was calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air. The

identity of the material as a member of the M41S class is confirmed from its properties.

The M41S crystalline product was formulated into a palladium-containing catalyst by the following method. A 5 sample of the as-synthesized M41S material was ammonium exchanged and dried at 120°C overnight. The sample was extruded with alumina, dried overnight at 120°C and calcined in nitrogen for 6 hours at 480°C and in air for 12 hours at 540°C. The calcined sample was impregnated with 10 $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution (about 1 wt% Pd) and then calcined at 300°C in air for 3 hours.

EXAMPLE 2

The catalyst of Example 1 and the following conventional catalysts were used to hydrogenate a 15 hydrotreated base stock with the characteristics given in Table 2:

- a) a commercial nickel catalyst on a silica/magnesia support as supplied by Engelhard Corporation (composition 31 wt% Ni, 32 wt% NiO, 24 wt% amorphous silica and 13 wt% 20 MgO); and
- b) $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst.

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TABLE 2
Properties of Hydrotreated Basestock

| | UV Absorption Level | Liters g ⁻¹ m ⁻¹ (X1000) |
|----|----------------------------------|---|
| 5 | 226 nm | 368 |
| | 254 nm | 16.6 |
| | 275 nm | 32.7 |
| | 325 nm | 1.29 |
| | 400 nm | <.1 |
| 10 | Sulfur, wt% | <0.002 |
| | Nitrogen, ppm | 2 |
| | Kinematic Viscosity, cS @ 40°C | 26.75 |
| | Kinematic Viscosity, cS @ 100°C | 4.87 |
| 15 | Simulated <u>Distillation</u> | |
| | | °F °C |
| | Initial Boiling Point | 514 268 |
| | 1% Distilled | 570 299 |
| | 5% Distilled | 639 337 |
| | Final Boiling Point | 957 513 |

20 * UV absorption is a measure of the amount of aromatics present - these features are proportional for the limited range over which the data is presented.

The properties of the three catalysts are summarized in Table 3 below.

25

TABLE 3
**Relative Properties of the Catalysts Employed
In Example 2**

| | Catalyst | Ni/silica-magnesia Englehard | Pt/Al ₂ O ₃ | Pd/M41S/ Al ₂ O ₃ |
|----|------------------|---------------------------------|-----------------------------------|--|
| 30 | Metal | wt% | | |
| | Palladium | | | 0.81 |
| | Platinum | | | 0.89 |
| | Nickel | 56 | | |
| 35 | Pore diameter | Å 83 | 150 | 60 |
| | Surface Area | m ² /g 250 | 234 | 614 |
| | Real Density | g/cc 4.59 | 3.256 | 2.38 |
| | Particle Density | g/cc 1.35 | 0.842 | 0.75 |
| | Pore Volume | cc/g 0.523 | 0.881 | 0.92 |

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Pd/M41S contains 65 wt% M41S and 35 wt% alumina prior to the metal addition.

All catalysts were evaluated in a fixed bed pilot unit. A base stock with the characteristics given in Table 5 2 was used as the feed.

Table 4, below illustrates three different sets of data.

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TABLE 4

**Relative Characteristics of White Oils
Produced by the Catalysts of Example 4**

Case I

In Case I, pressure was varied. It was decreased substantially when Pd/M41S was used. Temperature and space velocity were held constant or only slightly varied for each catalyst. The temperature was held between 230-260°C (450-500°F), and LHSV was held between 0.25 and 1.0 LHSV. Pressure for Ni/silica-alumina and Pt/Al₂O₃ was held at about 14235 kPa (2050 psig), but for Pd/M41S it was lowered, first to 12170 kPa (1750 psig), then to 10445 (1500 psig). The products were measured for total aromatic content (UV signal at 325-400 nm). The UV absorption data indicates similar levels of polynuclear aromatics (PNA) and total aromatic content for Pd/MCM-41 and Ni/silica-alumina. White oils produced using Pt/Al₂O₃ had a much higher level of aromatics. Figure 1 illustrates the lowest UV absorption value being that obtained by using Pd/M41S at 12170 kPa (1750 psig).

Case II

In Case II, space velocity (LHSV) was varied significantly for Pd/M41S. It was approximately double the space velocity used for Ni/silica-alumina and Pt/Al₂O₃ in one run involving Pd/M41S and quadruple the space velocity used for Ni/silica-alumina and Pt/Al₂O₃ in a second run involving Pd/M41S. The temperature was held between 230-260°C (450-500°F). The pressure was held between 15270-15960 kPa (2200-2300 psig) for each catalyst, including Pd/M41S in the instance in which the space velocity was doubled. In the instance in which the space velocity was quadrupled, pressure was decreased to 10445 (1500 psig). At higher space velocity and lower pressure, Pd/M41S produced a product with UV absorption levels similar to those of Ni/silica-alumina at 0.25 LHSV. Therefore Pd/M41S produces a white oil similar in characteristics to that of the nickel catalyst, i.e. both are low in total and polynuclear aromatics. Pd/M41S operates at far less severe

conditions. There is little difference, however, between the aromatics content of the oil produced using Pd/M41S at 15270 kPa (2200 psig) and the aromatics content of the oil produced using Pd/M41S at 10445 (1500 psig). Lower pressures are therefore preferred. Figure 2 presents a graphical comparison of the catalysts and conditions.

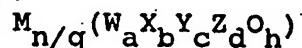
Case III

In Case III, the temperature was increased slightly and the pressure also increased in the run involving Pt/Al₂O₃. These conditions were more severe than those employed in the case of the nickel catalyst or Pd-M41S, yet the oil produced employing Pt/Al₂O₃ contains more aromatics than the oil produced using either of the other catalysts. Figure 3 illustrates the relative effects of temperature variation for the three catalysts involved.

CLAIMS:

1. A process for hydrogenating a lubricant hydrocarbon to produce a food grade white oil, said process comprising contacting a hydrocarbon lubricant feed in the presence of hydrogen with a hydrogenation catalyst containing a metal hydrogenation catalyst on a support, the support comprising an inorganic, non-layered, porous, crystalline phase material having pores with diameters of at least about 13 Å and exhibiting, after calcination, an X-ray diffraction pattern with at least one d-spacing greater than about 18 Å with a relative intensity of 100.
5
2. A process as claimed in claim 1 in which the crystalline phase material of the hydrogenation catalyst exhibits, after calcination, a hexagonal arrangement of uniformly sized pores with diameters of at least about 13 Å and which exhibits, after calcination, a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than
10 about 18 Å.
15
3. A process as claimed in claim 1 or claim 2 in which the crystalline phase material exhibits a benzene adsorption capacity of greater than about 15 grams benzene per 100 grams at 50 torr and 25°C.
20

4. A process as claimed in any preceding claim in which the crystalline phase has a composition expressed as follows:



5 wherein M is one or more ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; W is one or more divalent elements; X is one or more trivalent elements; Y is one or more tetravalent elements; Z is one or more pentavalent elements; a, b, c, and d are mole fractions of W, X, Y, and Z, respectively; h is a number of from 1 to 2.5; and (a+b+c+d) = 1.

10 5. A process as claimed in claim 4 wherein W comprises a
15 divalent first row transition metal or magnesium; X
comprises aluminum, boron, gallium or iron; Y
comprises silicon or germanium; and Z comprises
phosphorus.

20 6. A process as claimed in claim 4 wherein a and d are 0
and h = 2.

7. A process as claimed in claim 6 wherein X comprises
aluminum, and Y comprises silicon.

25 8. A process as claimed in any preceding claim wherein
the catalyst comprises at least one metal of Groups
VIA, VIIA or VIIIA of the Periodic Table.

30 9. A process as claimed in any preceding claim in which
the feed is contacted with the catalyst at a pressure
of 3550 to 20800 kPa (500 to 3000 psig), a temperature
from 120 to 370 °C (250 to 700°F), and a space
velocity from 0.1 to 2.0 LHSV.

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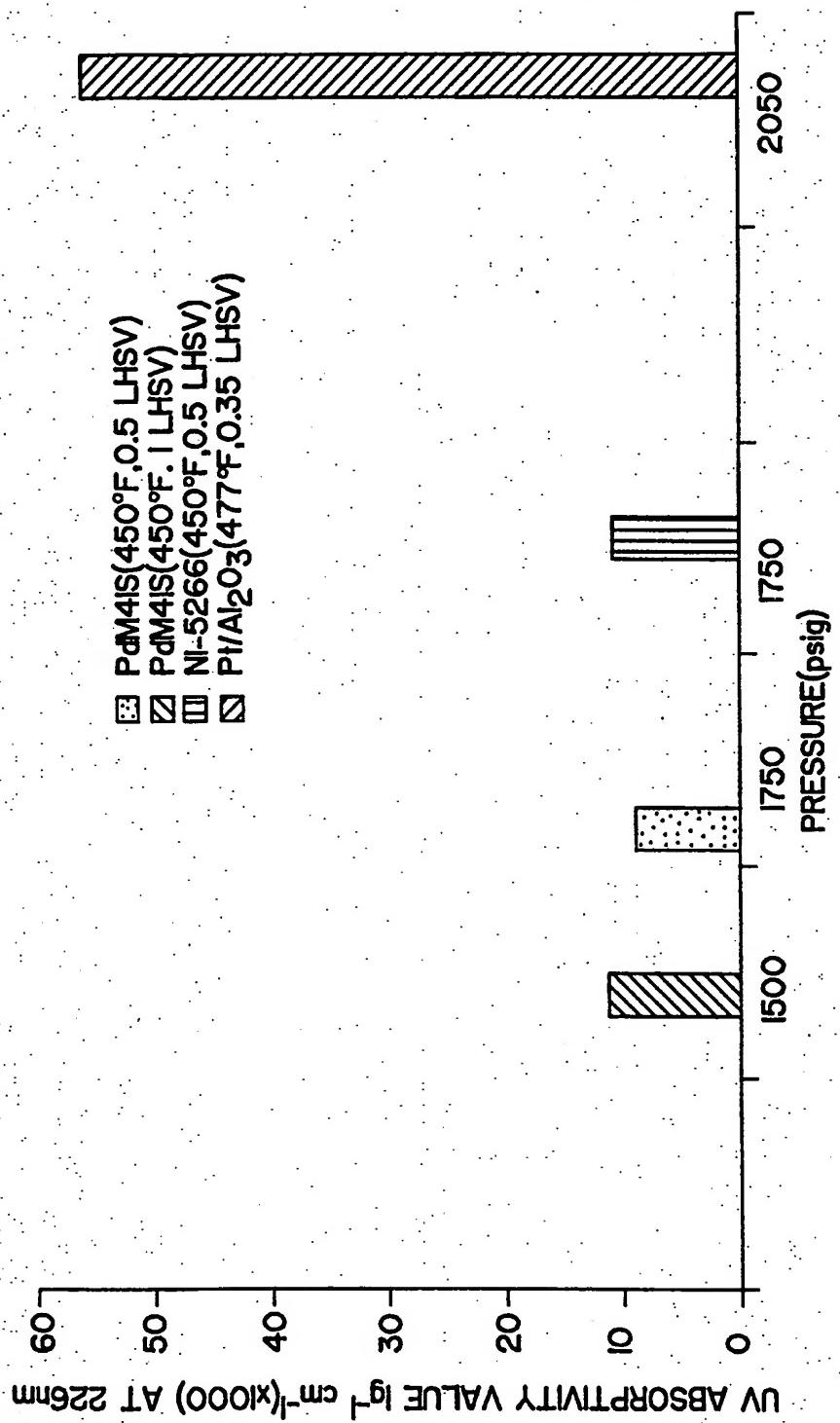


FIG. I

2 / 3

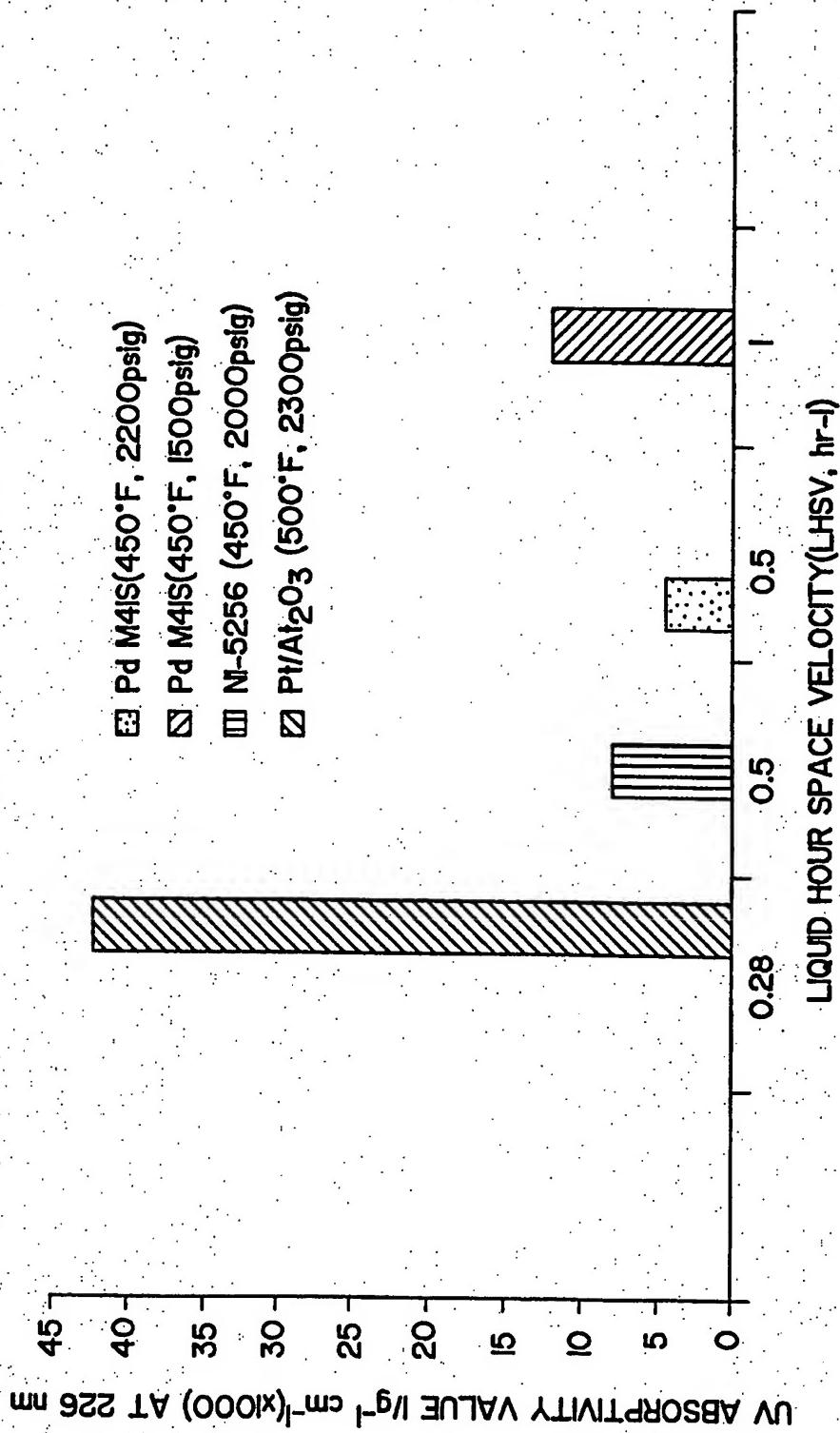


FIG. 2

3 / 3

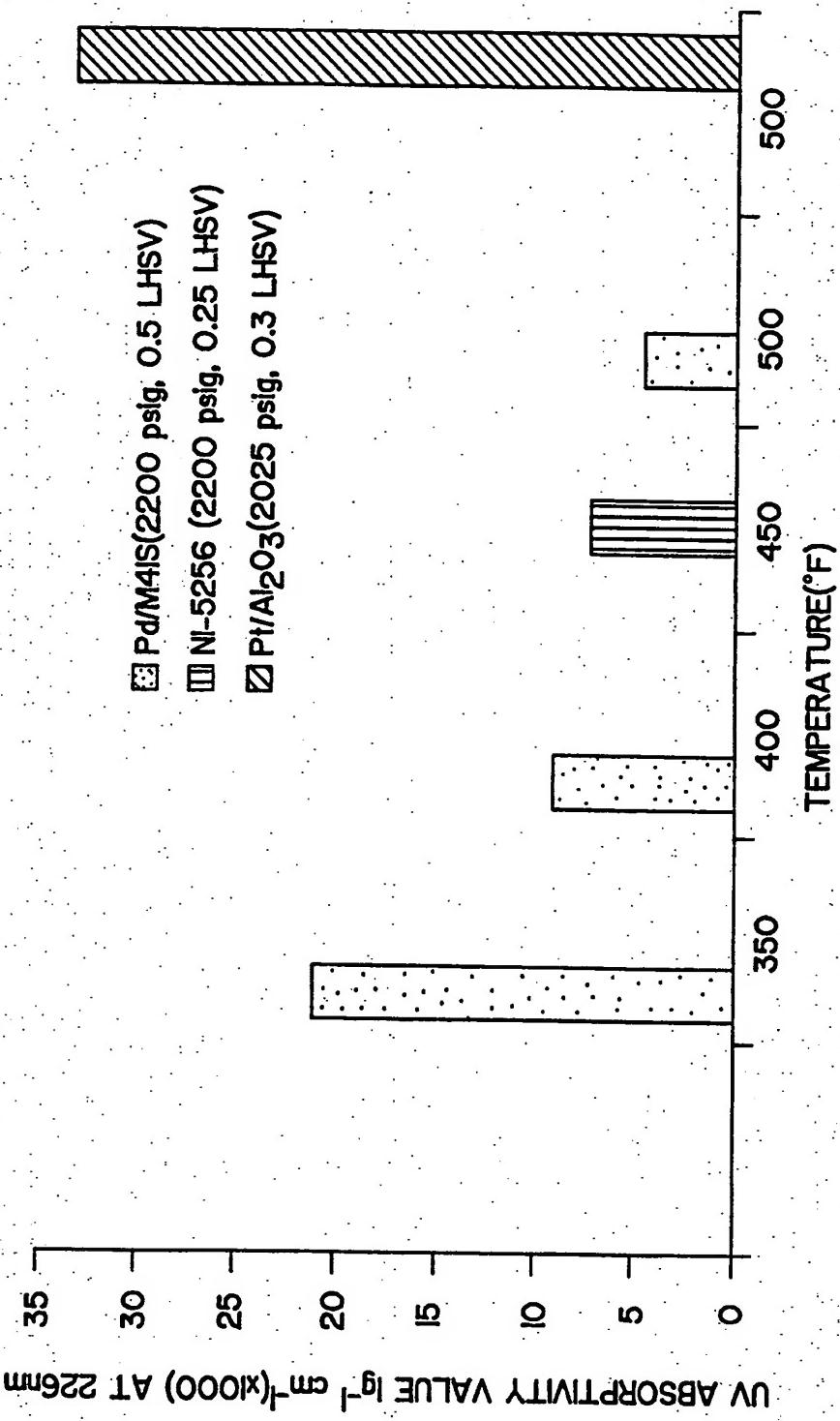


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/14412

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10G 45/04

US CL : 208/143

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/143

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

SEARCH TERMS: HYDROGENATION AND MCM 41

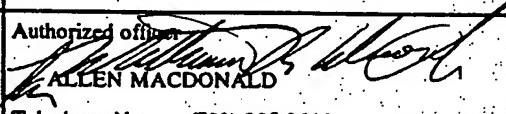
C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|--------------------------|
| Y | US, A, 5,134,241 (LE et al) 28 July 1992, col. 2, lines 29-45 | 1-9 |
| Y | US, A, 5,264,641 (Borghard et al) 23 October 1991, col 6, lines 10-64. | 1-9 |
| Y | US, A, 5,227,353 (Apelian et al) 13 July 1993, col 6, lines 10-64. | 1-9 col. 5, lines 16-55. |
| Y,P | US, A, 5,290,744 (Degnan Jr., et al) 01 March 1994, col. 1 lines 33 to col. 2 line 50. | 1-9 |

Further documents are listed in the continuation of Box C. See patent family annex.

| | | |
|---|----|--|
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| *E* earlier document published on or after the international filing date | Y* | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
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| *P* document published prior to the international filing date but later than the priority date claimed | | |

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| Date of the actual completion of the international search | Date of mailing of the international search report |
| 23 FEBRUARY 1995 | 28 MAR 1995 |

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| Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230 | Authorized officer  ALLEN MACDONALD Telephone No. (703) 305-9646 |
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